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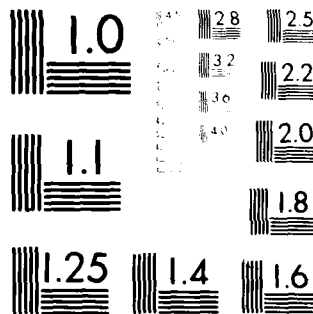
CONSTRUCTION ENGINEERING RESEARCH LAB (ARMY) CHAMPAIGN IL F/G 13/1
SELECTION OF COOLING WATER TREATMENT AT MILITARY INSTALLATIONS --ETC(U)
JUN 80 R LANE, A KUMAR
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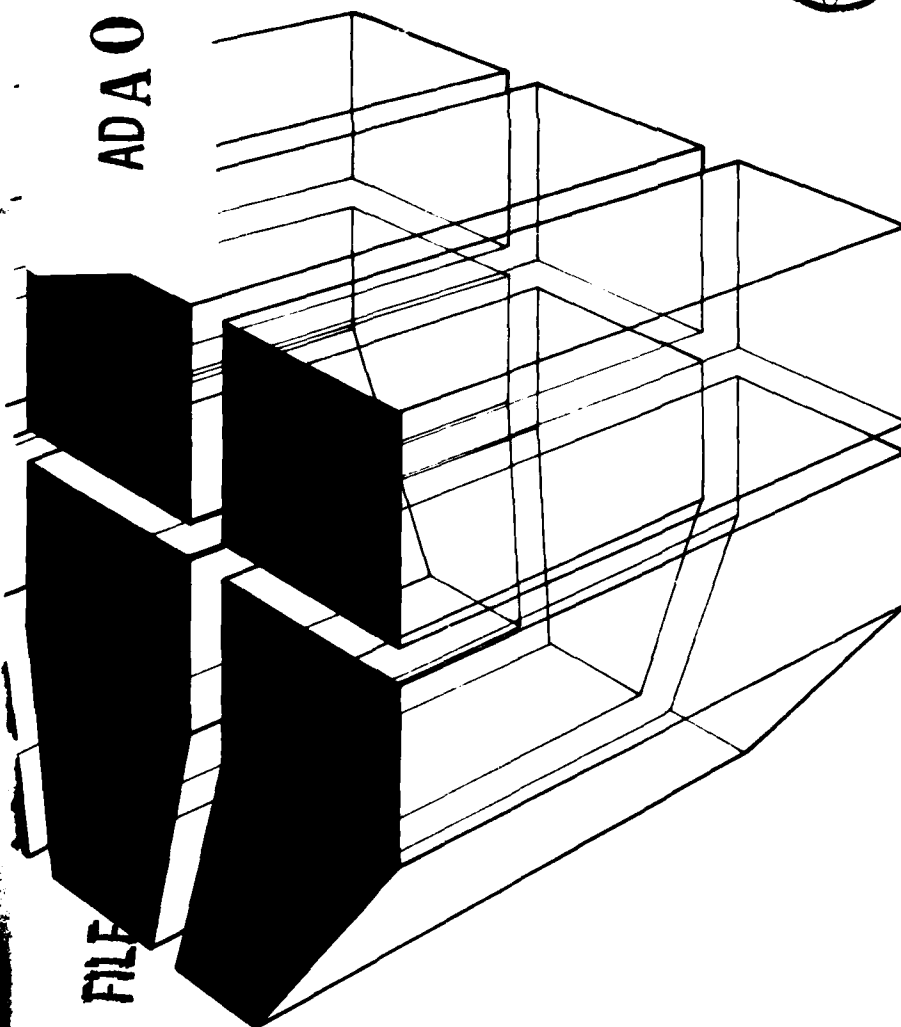
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TECHNICAL REPORT M-280
June 1980

SELECTION OF COOLING WATER TREATMENT
AT MILITARY INSTALLATIONS TO PREVENT
SCALING AND CORROSION

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by
R. Lane
A. Kumar

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Block 20 continued.

Training and Doctrine Command and U.S. Army Forces Command installations varies from 504 to 45,640.

The State of Illinois has tested recently developed treatment products made by commercial enterprises. The simplest method of cooling tower treatment is blowdown control. A reciprocating cooling tower evaporates 1.5 gallons of water per hour per ton (5.67 gal/0.9 MT), while an absorber evaporates 3 gal/hr/ton (11.12 gal/0.9 MT). The blowdown rate equals the evaporation rate divided by, cycles of concentration minus 1. The makeup water equals the amount of evaporation plus blowdown. The maximum cycles of concentration are limited by the scaling chemicals in the water; it is considered uneconomical to run less than 3 cycles of concentration. For cooling towers less than 20 tons (18.1 MT), the water should be air cooled or passed once only. For cooling towers of 20 to 50 tons (18.1 to 45.3 MT), 3 cycles of concentration with sodium hexametaphosphate (0.5 to 5 ppm) should be used. For cooling towers larger than 50 tons (45.3 MT), the treatments shown in Table 3 should be used. For hard water, if the scaling product is more than 20,000, sulfuric acid should be used to reduce alkalinity, and then the chemicals shown in Table 3 added. For sulfuric acid feed, Eq 4 should be used.

The maximum cycles of concentration should not exceed $150 \div Si$ (ppm) or

$$\sqrt{\frac{110,000}{Ca \times M}}$$

The concentration of phosphate should not exceed 7 ppm, and that of item 2 phosphonate should not exceed

$$\sqrt{\frac{110,000}{Ca \times M}}$$

Otherwise, phosphate or phosphonate scale will precipitate.

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FOREWORD

This investigation was conducted by the U.S. Army Construction Engineering Research Laboratory (CERL) for the U.S. Army Training and Doctrine Command (TRADOC) under reimbursable Inter-Army Order Number GEFAE 230400100. Partial funding was also provided by the U.S. Air Force Engineering and Services Center, and Headquarters, U.S. Army Forces Command. The investigation was conducted by the Engineering and Materials Division (CERL-EM). Dr. A. Kumar was the CERL principal investigator, and Mr. A. Bettcher of TRADOC was the technical monitor. The assistance of Mr. M. McLeod of the U.S. Army Facilities Engineering Support Agency (USAFESA) is acknowledged.

Dr. G. R. Williamson is Chief of EM. COL L. J. Circeo is Commander and Director of CERL, and Dr. L. R. Shaffer is Technical Director.

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SELECTION OF COOLING WATER TREATMENT AT MILITARY INSTALLATIONS TO PREVENT SCALING AND CORROSION

1 INTRODUCTION

Background

Cooling towers or evaporative condensers are water-saving devices that provide cooled water for air-conditioning or refrigeration systems. Instead of employing costly once-through cooling water, the cooling tower system recirculates water through an aeration system called the cooling tower, where it is cooled by evaporation, and then returns it to the heat exchanger.

Each year, the heat transfer efficiency loss attributed to scaling and corrosion damage to metal and wooden cooling tower components costs the Army and the Air Force thousands of dollars. To prevent such problems, the level of total dissolved solids and other fouling materials in cooling tower water must be limited. However, a level of dissolved solids that is too low would not only waste water but could also be corrosive to the metallic components of the cooling tower. A thin layer of scale deposited on the metallic surfaces is, in fact, useful because it protects the metallic surfaces from corrosion caused by water.

A water treatment program must address scaling, corrosion, and fouling problems in the cooling tower structure and equipment. Currently, there is no Army-wide guidance for cooling tower water treatment. Individual Army installations have contracts with different companies to provide chemicals and feeding equipment. In some cases, two or three companies have contracts on the same installation. These chemicals are bought on "sole source" contract because the chemical compositions are proprietary.

The Army has recognized a need to identify the various causes of scaling, corrosion, and fouling in cooling tower systems at military installations, and to provide Facilities Engineers with standardized methods to prevent and control these problems.

Objective

The objective of this report is to identify the causes of, and offer solutions for scaling, corrosion, and fouling in cooling tower systems.

Approach

Cooling water treatment formulations which have been proven in the laboratory and the field, water treatment feed and blowdown control equipment, scaling indices and scale-preventing chemicals, and experimental formulations which are more environmentally acceptable were investigated (Chapters 2, 3, and 4). Inhibitors can control corrosion in the cooling tower structure; typical corrosion inhibitors which have been used successfully in cooling tower systems were examined (Chapter 5). These data provided a basis for guidance on cooling tower water treatment to control scale and corrosion. The appendix provides general corrosion principles used in analyzing corrosion problems in cooling towers.

Mode of Technology Transfer

The information in this report will form the basis for a draft technical bulletin on cooling tower water treatment at Army installations and will also impact the revision of TM 5-810-1, *Mechanical Design, Heating, Ventilating and Air Conditioning*.

2 WATER TREATMENT FORMULATIONS

Scaling and Corrosion Problems

In a cooling tower, the water is cooled by counter-current air flow, which evaporates the water droplets passing down through openings in the distribution deck. One percent of the circulating water passing through a cooling tower is evaporated for each 10°F (5.5°C) temperature decrease. A cooling tower evaporates 1.5 gal/hr/ton (5.67 l/0.9 MT) in centrifugal or reciprocating air conditioning, and 3 gal/hr/ton (11.24 l/0.9 MT) in absorber air conditioning. The water flows over wood or plastic slats to the tower basin (see Figure 1). Usually, there is an 8° to 15°F (-13° to +9°C) temperature decrease in the water as it passes through the tower; it is then returned from the tower to the heat exchanger.

During evaporation, minerals remain in the circulation water, thus making it more concentrated than the makeup water, often to the point of saturation. "Cycles of concentration" (COC) is the term comparing the concentration of circulating water to the makeup water. If the circulating water has three times the concentration of minerals of the makeup water, the COC is 3. Scaling is the precipitation of dense, adherent material on heat exchanger surfaces. Precipitation

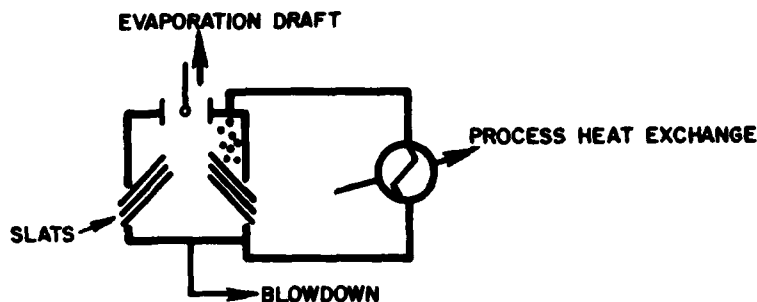


Figure 1. Typical induced-draft open recirculating cooling tower.

of scale-forming salts occurs when solubilities are exceeded because of high concentrations or increased temperature (see Figure 2).

Natural windage loss and blowdown or bleedoff are used to determine the amount of makeup water needed to reduce the salts concentration. Blowdown removes a portion of the concentrated circulating water; this water is replaced with fresh makeup water, which lowers the COC. Both continuous or intermittent blowdown can be used. While blowdown is an effective way to reduce and limit the COC, and therefore the scaling potential of the circulating water, excessive rates of blowdown may not be tolerable because of the cost of the increased amount of water used—especially if supplies of fresh water are limited. Enough blowdown to maintain about 4 COC is commonly prescribed, although the quality of the makeup water, pH, alkalinity, amount of total solids, and the efficiency of the water treatment may determine the allowable COC. The COC can be measured from the total dissolved solids (TDS) content as determined by conductivity of the cooling tower water and the makeup water. COC can be expressed as:

$$\text{COC} = \frac{\text{MU}}{\text{B}} = \frac{\text{E} + \text{B}}{\text{B}} \quad [\text{Eq 1}]$$

where MU is the quantity of the makeup water which is the sum of evaporation, E, and blowdown, B. Therefore,

$$\text{B} = \frac{\text{E}}{\text{COC} - 1} \quad [\text{Eq 2}]$$

and

$$\text{MU} = \frac{\text{E} \times \text{COC}}{\text{COC} - 1} \quad [\text{Eq 3}]$$

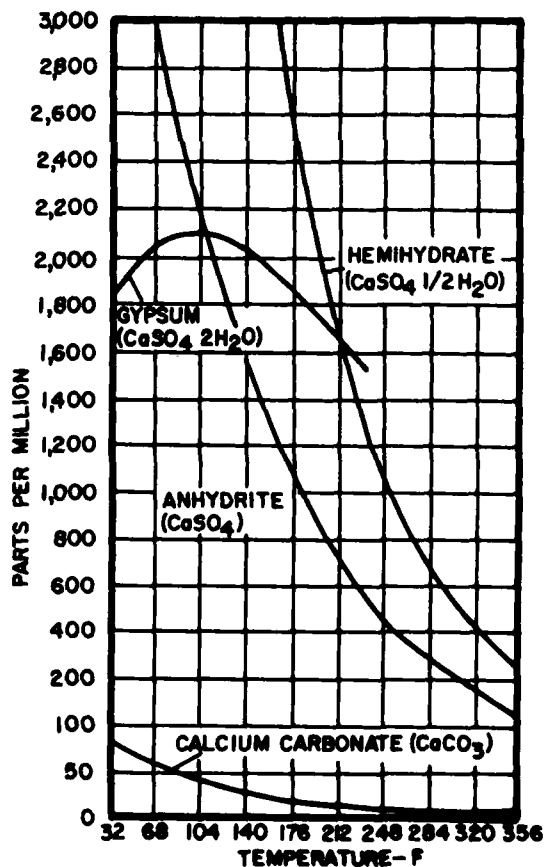


Figure 2. Solubility of calcium carbonate compared to calcium sulfate. (From *Handbook of Industrial Water Conditioning*, 7th ed. [Betz Laboratories, Inc., 1976].)

In the past, cooling water treatment consisted mainly of adding sodium zeolite softening or blended polyphosphate-lignosulfonate mixtures for waters with lower levels of hardness, and acid plus chromate for the harder waters. Recently, superior organic scale inhibitors—such as the phosphonates, acrylates, and maleates—and satisfactory corrosion inhibitors employing synergistic combinations of zinc, phosphonates, azoles, and molybdates either alone or in combination with lower chromate levels have been used successfully. Table 1 shows the specifications for chemicals that have commonly been used in Illinois State institutions for cooling tower treatment.

Scaling in some waters can be prevented just by reducing the maximum COC. If the calcium (Ca) and methyl alkalinity (M) is known, then the maximum COC should be less than

$$\sqrt{\frac{110,000}{\text{Ca} \times \text{M}}}$$

This type of treatment is limited to the low to medium hardness waters, since operating below 3 COC is usually considered uneconomical. Where silica is present, the maximum COC has an absolute limit of $150 \div \text{Si}$ (ppm).

Army bases often have many small air-conditioning installations; since manpower for servicing these facilities may be limited, a simpler treatment method, consisting of liquid blended formulations, can be used. Laboratory and field tests in Illinois State institutions have shown that the following liquid formulations provide reasonable scale and corrosion inhibition in cooling tower waters.

1. Liquid Cooling Tower Treatment, Blend L (Item 2* of Table 1), consists of 12 percent diphosphonic acid (as Item 3), 2 percent zinc chloride anhydrous (ZnCl_2), and 86 percent softened water. This liquid treatment contains less than 0.1 percent insoluble matter, and the pH of its solution should be approximately 2 to 3 at room temperature. The use of 0.3 lb (.12 kg) of this formulation per 1000 gal (4108 l) of makeup water is recommended for treating water with 4 COC.

*These data were compiled from the Illinois Department of Administrative Services' publication, *Standard Specification for Boiler Compound and Water Treating Chemicals and Water Testing Reagents and Supplies* (February 1, 1978). All item numbers refer to chemical composition specified in Table 1.

2. Liquid Cooling Tower Treatment Blend M (Item 8), consists of 9.5 percent disphosphonic acid (as Item 3), 4.8 percent caustic soda (as Item 9), 2.8 percent sodium pyrophosphate (as Item 10), 1.4 percent causticized mercaptobenzothiazole, and 81.5 percent softened water. This liquid treatment contains less than 0.1 percent insoluble matter, and the pH of its solution should be approximately 10 at room temperature. The use of 0.4 lb/1000 gal (.16 kg/4108 l) of makeup water is recommended for treating water with COC.

3. Liquid Cooling Tower Treatment, Blend P (Item 14 of Table 1) consists of 20 percent aminotri (methylenephosphonic) acid, 12.6 percent disodium phosphate anhydrous, and 67.4 percent softened water. For treating water with a COC of 4, 0.2 lb (.0908 kg) of this formulation per 1000 gal (4108 l) of makeup water is recommended. This liquid treatment should contain less than 0.1 percent insoluble matter, and the pH of its solution should be approximately 2 to 4 at room temperature.

An empirical evaluation of the scaling tendency of the supply water is shown by the product of the calcium (Ca) and alkalinity (M); this is defined as the scaling product (SP). These formulations (Blends L, M, O and P) are designed to treat waters with a low level of hardness ($\text{SP} < 20,000$), however, Item 8 (Blend M) may also inhibit corrosion when used with an acid-type treatment for waters having a high level of hardness ($\text{SP} > 20,000$), but it must be applied separately.

Recommended treatment methods for Army installations in Table 2 have been based on representative water analyses of 20 U.S. Army Training and Doctrine Command (TRADOC) and U.S. Army Forces Command (FORSCOM) posts taken by the U.S. Army Environmental Hygiene Agency.* It is preferable to use the SP based on actual water composition at the Army post since the water is from many sources and has changing composition.

It is more economical to purchase individual concentrated chemicals and a minimum of blends. Blends that consist of two or more chemicals in liquid form (often containing 30 to 90 percent water) are much more costly because of their dilute composition, the

*Summary of U.S. Army Drinking Water Surveillance Program Data Base (U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD, 1977).

Table 1
A List of Chemicals for Cooling Tower Water Treatment
(From Standard Specification for Boiler Compound & Water Treating Chemicals and Water Treating Reagents and Supplies
[Illinois Department of Administrative Services, February 1, 1978])

Item No. as Listed in This Report	Item No. as Listed in Ill. Dept. of Admin. Services Publications	Chemical	pH	Specific Gravity	Packaging	Units*	Special Characteristics
1	61	Sodium bichromate or sodium dichromate - ($\text{Na}_2\text{Cr}_2\text{O}_7$) $2\text{H}_2\text{O}$, 99.8%			100-lb paper bags	lb	Technical, granular
2A	84	Pentasodium Aminotri- (methylphosphonate)- ($\text{Na}_5\text{O}_3\text{PH}_2\text{C})_3\text{N}(\text{CH}_2\text{PO}_3\text{Na})_3$), 39-41%.	10.0 to 11.0 in 1% solution	1.42 (20°C/15°C)	15-gal (170 lb), polyethylene-lined nonreturnable steel drums	lb	Prevents precipitates when used at threshold dosages (2 to 20 ppm) in cooling water, as Dequest 2006** or equivalent
2B	84	Same as Item 2A			55-gal (600-lb) polyethylene-lined nonreturnable steel drums	lb	
2C	84	Same as Item 2A			5-gal (approximately 55-lb) polyethylene- lined steel pails	lb	
3A	95	Diphosphonic acid formula - (1-hydroxyethylidene, 1, 1-diphosphonic acid) for prevention of scale in cooling water: active ingredient 58-62%	Less than 2.0 in 1% solution as Dequest 2010,** or equivalent	1.45 at 20°C/15°C)	15-gal (170-lb net) polyethylene-lined nonreturnable steel drums	lb	
3B	95	Same as Item A			55-gal (600-lb net) polyethylene-lined nonreturnable steel drums	lb	

Table 1 (cont'd)

Item No. as Listed in This Report	Item No. as Listed in Ill. Dept. of Admin. Services Publications	Chemical	pH	Specific Gravity	Packaging	Units*	Special Characteristics
4A	108	Biocidal agent blend; shall contain: N-Alkyl (C ₁₂ - 5%, C ₁₄ - 60%, C ₁₆ - 30%, C ₁₈ - 5%), dimethyl benzyl ammonium chloride, 23-25%	Greater than 10.5	0.98 (65°F)	5-gal (40-lb net) non- returnable steel pails with pour spout	lb	Controls slime-forming microorganisms in cool- ing water systems When applied at the rate of 0.1 to 0.75 lb/1000 gal, should be effective in con- trolling slime
4B	108	Bis (Tributyltin) oxide 4-6% Inert ingredients, such as solubilizing and dispersing agents, 70-72%			30-gal (250-lb net) nonreturnable steel drums	lb	
5A	112	Causticized mercaptobenzo- thiazole - (C, H ₄ , NS ₂ , Na), corrosion inhibitor for copper; 50% aqueous solution, such as Nacap** or equivalent			5-gal (40-lb) steel containers	lb	
5B	112	Same as Item 5A			55-gal nonreturnable drums (575 lb net)	lb	

*Metric conversion factors: 1 lb = 4 kg; 1 gal = 4.108 L; °C = °F - 32 × 5/9

**A registered trademark of the Monsanto Chemical Co.

Table 1 (cont'd)

Item No. as Listed in This Report	Item No. as Listed in Ill. Dept. of Admin. Services Publications	Chemical	pH	Specific Gravity	Packaging	Units*	Special Characteristics
6	115	Cooling Tower Treatment, Blend H, corrosion inhibitor Sodium chromate, 63-67% Sodium pyrophosphate, 33-37%			50-lb quantities in moisture-proof bags or in (400-lb net) fibre drums of proper mech- anical strength and chemical resistance	lb	Uniform mixture; readily dissolves in water; contains no more than 0.5% insoluble matter
7	137	Liquid Cooling Tower Treatment, Blend L, for prevention of scale and corrosion in cooling tower waters Diphosphonic acid, 12% Zinc chloride, anhydrous (ZnCl ₂), 2% Softened water, 86%	Approximately 2 to 3 in solution at room temperature		30-gal (est. 285 lb) Rotationally molded drums with fibre overpak	lb	Contains less than 0.1% insoluble matter
8	138	Liquid Cooling Tower Treatment, Blend M, for prevention of scale and corrosion in cooling tower waters Diphosphonic acid, 9.5% Caustic soda, 4.8% Sodium pyrophosphate, 2.8% Causticized mercaptobenzothiazole, 1.4% Softened water, 81.5%	Approximately 10 in solution at room temperature		30-gal (est. 300-lb) rotationally molded drums with fibre overpak	lb	Contains less than 0.1% insoluble matter
9	4	Caustic Soda (NaOH), flake or beads, 76% (Na ₂ O)			Steel drums, 400 lb net	lb	

Table 1 (cont'd)

Item No. as Listed in This Report	Item No. as Listed in III. Dept. of Admin. Services Publications	Chemical	pH	Specific Gravity	Packaging	Units*	Special Characteristics
10	18	Tetrasodium Pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$), anhydrous, 53% P_2O_5			Granular, in 100-lb, moisture-proofed paper bags	lb	
11A	46	Calcium hypochlorite ($\text{Ca}(\text{OCCl})_2$); contains approximately 70% avail- able chlorine by weight			5-lb cans	lb	Should be a white or yellowish-white granular powder, free from lumps, dirt, or foreign material
11B	46	Calcium hypochlorite ($\text{Ca}(\text{OCCl})_2$); contains approximately 70% avail- able chlorine by weight			100-lb metal drums	lb	Should be a white or yellowish-white granular powder, free from lumps, dirt, or foreign material
12	141	Zinc chloride (ZnCl_2)				lb	
13		Liquid Cooling Tower Treatment, Blend O, for prevention of scale and corrosion in cooling tower waters contains: Aminotri (methylene- phosphonic acid), 60% Zinc chloride, anhydrous, 14% 100% hydrochloric acid, 6.6% Softened water, 29.4%	Approximately 2 to 3 in solution at room temperature			lb	.07 lb of this formulation per 1000 gal of makeup water is recommended for treating water having a COC of 4; contains less than 0.1% insoluble matter This blend has problems in storage and therefore is not recommended

*Metric conversion factors: 1 lb = .4 kg; 1 gal = 4.108 g; $^{\circ}\text{C} = ^{\circ}\text{F} - 32 \times 5/9$

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Table 1 (cont'd)

Item No. as Listed in This Report	Item No. as Listed in Ill. Dept. of Admin. Services Publications	Chemical	pH	Specific Gravity	Packaging	Units*	Special Characteristics
14		Liquid Cooling Tower Treatment, Blend P, for prevention of scale and corrosion in cooling tower waters consists of: Aminotri (methylene- phosphonic acid), 20% Disodium phosphate, anhydrous, 12.6% Softened water, 67.4%	Approximately 2 to 4 in solution at room temperature		50-lb quantities in moisture-proof bags or in (400-lb net) fibre drums of proper mechanical strength and chemical resistance	lb	0.2 lb (.008 kg) of this formulation per 1000 gal (4108 l) of makeup water is recommended for treat- ing water with a COC of 4; should contain less than 0.1% insoluble matter
15	64	Cooling Tower Treatment, Blend C, for prevention of corrosion in cooling tower waters Sodium bichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$), 86-90% Zinc sulfate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$), 10-14%				lb	Should be a uniform mix- ture which readily dissolves in water and does not con- tain more than 0.5% insoluble matter

*Metric conversion factors: 1 lb = .4 kg; 1 gal = 4.108 l; °C = °F - 32 × 5/9

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Table 2

Chemical Composition of Treated or Distribution Waters at FORSCOM and TRADOC Army Commands
(These data were taken from *Summary of U.S. Army Drinking Water Surveillance Program Data Base*
[U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD, 1977])

FORSCOM	Cu	Fe	Mg (as CaCO ₃)	Mn	M (as CaCO ₃)	pH	Hardness H (as CaCO ₃)	Conduct- ivity (umhos/cm)	Ca (as CaCO ₃)	SiO ₂	Cl	SO ₄	Scaling Product (SP) Aver. Ca x M (both as CaCO ₃)
Ft. Bragg, NC	.03	.1-1	2-9	.03-.06	2-40	5-7.2	6-30	20-250	3-45	0-6	2-5	3-13	504
Ft. Carson, CO	.1-2	.1-7	45-194	.03	106-175	7.4	166-722	900-1400	108-543	13-32	11-22	91-400	45,640
Ft. Hood, TX	.03	.2	37	.03	132-347	7.9	63-161	360-2100	28-115	6-9	32-447	27-301	17,203
Ft. Sam Houston, TX	.04	.1-7	132	.03-.2	260-320	7.9	307-411	600-800	245-290	10	9-26	23-94	77,720
Ft. McPherson, GA	.03	.1	10-18	.03	40-77	7.0-7.4	30-72	100-200	18-28	23-30	32	3	1334
Ft. Ord, CA	.03	.1-5	91	.03-.08	112-179	7.3	227-275	650-780	148-163	38-45	38-126	71-97	18,876
Ft. Polk, LA	.03	.2	8	.05	56-174	7.2	45-106	300	35-128	30-46	19-25	3-10	9430
SF Presidio, CA	.1-2	.1-6	16-152	.03	76-152	7.5-8.1	40-218	240-560	28-70	9-23	18-44	19-49	5586
Ft. Riley, KS	.03	.1	49-132	.04	270-360	7.4-8.6	320-385	700-800	213-258	16-34	6-27	40-100	74,340
Ft. Stewart, GA	.03	.1-2	33-49	.03	98-120	7.5-8.0	85-107	220-310	48-68	19-46	5-9	2-7	6322
TRADOC													
Ft. Belvoir, VA	.04-.1	.1	13	.03	39	7.1	70-81	190	65	4-9	4-11	22	2535
Ft. Benning, GA	.03-.04	.1-3	4-17	.03-.3	10-75	6.2-8.0	10-43	60-400	5-35	2-33	3-26	4-10	860
Ft. Bliss, TX	.03	.1	49	.03	145	7.8	150	500-740	90-120	23-32	82-130	59-98	15,225
Ft. Hamilton, NY	.06-.09	.1-6	4-10	.03	8.7	6.8	20	59	12	2.5	3.8	7.3	104
Ft. Jackson, SC	.03-.06	.1-2	2	.04	1-6	5.1-6.3	5-12	11-27	3-6	4-8	5-4	1-3	16
Ft. Knox, KY	.025	.1	72	.03	54	7.9	135	509	55	11	83	38	2970
Ft. Lee, VA	.025	.1-7	11	.04	17-25	6.8-7.6	49	143	28-38	12	10	19	693
Ft. Monroe, VA	.04	.1	7	.04	30	7.3	80	215	70	6	17	31	2100
Ft. Rucker, AL	.03-.06	.1-1	12-54	.03	109-168	7.7-8.2	90-160	260-310	50-105	12-35	1-15	4-11	10,764
Ft. Sill,* OK	.03-.15	--	--	--	116-128	7.1-7.4	144-171	350-430	124-135	13-14	17-35	--	15,860

*Lake Lanoka

mixing cost, double freight costs, and the company's overhead for doing the blending.

Generally, low to medium hardness water having an SP of less than 20,000 can be treated satisfactorily with .03 to .05 lb (.012 to .020 kg) of Item 2 pentasodium aminotri (methylene phosphonate) (SATMP), .01 lb (.004 kg) of Item 10 (sodium pyrophosphate), and .007 lb (.0028 kg) of Item 5 (causticized mercaptobenzothiazole) per 1000 gal (4108 l) of makeup water. The concentration of phosphate should not exceed 7 ppm, and the concentration of SATMP should not exceed

$$\sqrt{\frac{110,000}{\text{Ca} \times \text{M}}}$$

otherwise phosphate or phosphonate scale will precipitate. It should be recognized that the growth of algae, which can foul the cooling water system, is increased by the presence of phosphorous from phosphates and phosphonates. Water having an SP greater than 20,000 will require acid treatment plus chromate or nonchromate corrosion inhibitors.

The sulfuric acid (93 percent acid or 66° Baume) dosage (A) in pounds/1000 gal (kg/1720 l) of makeup is calculated as follows:

$$A = \frac{M - M^1}{120 \times \text{COC}} \quad [\text{Eq 4}]$$

where M^1 is the alkalinity of treated water (usually 40), and M is the alkalinity of the makeup water.

Overtreatment should be avoided, since it may cause serious corrosion of metallic components. One advantage of this treatment is that the scaling caused by undertreatment may be corrected by a short, carefully controlled overtreatment. A disadvantage of this method is that surface water supplies may vary in alkalinity, and the proportional method of treatment will not correct for such variations. In such cases, pH must be measured and controlled.

Table 3 shows the various treatment methods that can be applied.

Based on these guides, Army installations should use the treatments and proportioning equipment specified in Table 4. Whether treatment type D, E, or F (in Table 4) is prescribed should be based on: (1) the number and capability of available manpower to apply three separate chemicals to chemical vats, (2) the size

of conditioning equipment and the increased cost of applying liquid formulations (method F in Table 4), and (3) whether chromate treatment is permitted, even if it is only being applied to the sanitary sewer. Because chromate is a superior corrosion inhibitor, its use is encouraged, as long as the U.S. Environmental Protection Agency (USEPA) approves its application for a particular area.

For example, the scaling products of water supplies at Fort Bragg and Fort Carson are 504 and 45,640, respectively (Table 2). Tables 2 and 3 show that the water at Fort Bragg has low scaling tendencies and can have a COC of up to 8. Chemical treatments D, E, and F are recommended for Fort Bragg, as shown in Table 4. Chemical treatment F consists of a single liquid blend L (Item 7, Table 1). Chemical treatment D is even more economical, but requires additional manpower to apply three separate chemicals to chemical vats. Chemical treatment E involves the use of chromates and is very effective; however, the maximum allowable content of hexavalent chromium for disposal in a sanitary sewer is set at 5 ppm by the USEPA.

On the other hand, Fort Carson has a high level of water hardness, with a scaling product of 45,640 (Table 2). Tables 3 and 4 show that treatments G, H, and J can be used. Treatment J involves the addition of sulfuric acid to lower the alkalinity of the makeup water to 50 to 100 mg/l with the further addition of blend M or treatment D. Treatment H is similar in that sulfuric acid is used with the further addition of chromates, if permitted by the USEPA. However, if zeolite-softened makeup water is available, treatment G can be used. Treatment G contains chromates and should not be used if the USEPA does not allow chromate effluent.

Fouling Problems

In addition to scale and corrosion problems, algae and slime may grow in open circulating cooling water systems. Such growths may block air and water passageways, encourage the development of corrosion under the inorganic deposits, interfere with heat transfer in exchangers, and hinder evaporation, flow, and cooling tower efficiency. Sunlight and the presence of certain nutrients, such as phosphorous, encourage the growth of algae. Therefore, covering the top deck of the cooling towers to eliminate sunlight on the water surface will substantially reduce algae growth. In addition, manual application of Item 11 (calcium hypochlorite) to the tower deck (or, less preferably, to the basin) at the rate of about 2 oz/1000 gal

Table 3
Guidelines for Cooling Water Treatment at Army Bases
(Metric Conversion Factor: 1 lb = .4 kg; 1 gal = 4.108 l)

	Scaling Product (SP) $\text{Ca} \times \text{M}$ (both as CaCO_3)			Remarks
	<2,000	<20,000	>20,000	
Estimated COC	4-10	2-4	4-10	
Treatments (lb/1000 gal makeup water)				
D. .03-.05 lb, Item 2* .01 lb, Item 10 .007 lb, Item 5	OK	OK	No	Nonchromate
E. .03-.05 lb, Item 2 30-50 mg/l CrO_4 (in tower concentrate) as Item 6	OK	OK	No	Low Chromate
F. 0.33 lb, Item 7/1000 gal or 0.4 lb, Item 8/1000 gal	OK	OK	No	Nonchromate Blend
G. Zeolite softened makeup + 50-100 mg/l CrO_4 (in tower concentrate) as Item 1	OK	OK	OK	Chromate
H. H_2SO_4 to reduce M (alkalinity of makeup water) to 50-100 mg/l + Blend C to provide 30-50 mg/l chromate (as CrO_4) in cooling tower concentrate	Too complex a method of treatment for this water quality	Same	OK	Acid + Blend + Low Chromate
J. H_2SO_4 to reduce M of makeup water to 50-100 mg/l + treatment D above (preferable), or Item 8	Too complex a method of treatment for this water quality	Same	OK	Acid + Nonchromate

*All item numbers refer to chemical composition specified in Table 1.

(.05 kg/4108 l) of cooling system capacity one to three times weekly will usually control algae growth. Alternate application of Item 4A (biocide) will usually be even more beneficial. Periodic alternate application of Items 11 and 4 should provide the necessary germicidal action to prevent this problem. Algaecides or biocides should be applied separately from the other water treatment chemicals and should be fed in "slug"-type amounts to derive the optimum biocidal action. Chlorine biocides are not effective if the water pH is greater than 7.5.

The air-conditioning and treatment equipment of important facilities should be checked at least every 2 days if their capacity is greater than 100 tons (90.7 MT). The water should also be tested with portable equipment. Such small, portable testers allow the operator to conduct the tests at the site, adjust feeder and blowdown immediately, and check the chemical vat for refilling. It is essential that personnel keep and submit accurate records of the water tests, meter readings, and chemicals dissolved. More complete and accurate tests should be conducted at

Table 4
Recommended Proportioning Equipment and Treatment for Specific Army Bases

Base	Scaling Product (SP)	Treatment				Proportional Feed Equipment**
	Aver.	Estimated			Type (From Table 3)	
	Ca x M (as CaCO ₃)	Cycles	Hardness H (CaCO ₃)	Conductivity (μmhos/cm)		
Ft. Bragg	504	6-8	100-150	900-1200	D, E*, F	d
Ft. Carson	45,640	4-8	1800-3600	4500-9000	G*, H*, J	a or c
Ft. Hood	17,203	2	250	2500	D, E*, F	b or c
Ft. S. Houston	77,720	4-8	1450-2900	2800-5600	G*, H*, J	a or c
Ft. McPherson	1334	6-8	350-500	900-1200	D, E*, F	d
Ft. Ord	18,876	2	500	1500	D, E*, F	b or c
Ft. Polk	9430	3-4	250-300	900-1200	D, E*, F	b or c
SF Presidio	5586	3-4	400-500	1200-1600	D, E*, F	b or c
Ft. Riley	74,340	4-8	1400-2800	3000-6000	G*, H*, J	a or c
Ft. Stewart	6322	3-4	300-400	800-1000	D, E*, F	b or c
Ft. Belvoir	2535	4-6	300-450	800-1200	D, E*, F	d
Ft. Benning	860	6-8	200-250	1500-2000	D, E*, F	d
Ft. Bliss	15,225	2	150	1300	D, E*, F	b or c
Ft. Hamilton	104	6-10	70-120	400-600	D, E*, F	d
Ft. Jackson	10	6-10	70-120	150-200	D, E*, F	d
Ft. Knox	2970	4-6	550-800	2000-3000	D, E*, F	d
Ft. Lee	693	6-8	300-400	900-1200	D, E*, F	d
Ft. Monroe	2100	4-6	350-500	900-1400	D, E*, F	d
Ft. Rucker	10,764	6-8	750-1000	1800-2400	D, E*, F	b or c
Ft. Sill	15,860	2	350	800	D, E*, F	b or c

Purchase and installation of chemical proportioning equipment for small towers (<50 tons) may not be justified; application of slightly soluble phosphate plus weekly manual blowdown adjustment may be adequate.

*Should not be considered if CrO₄ effluent is not allowed; however, if EPA sampling of sanitary sewage outflow is where there is no evidence of CrO₄ detection, chromate treatment may be considered acceptable and is recommended because of its superior corrosion inhibition.

**Letters refer to methods listed on pp 16 and 17.

least weekly with burette-type testing equipment. It is also important to apply the algacides regularly, or it will be impossible to attain the desired amount of scale and corrosion inhibition and deposit-free surfaces.

3 WATER TREATMENT CONTROL AND BLOWDOWN CONTROL EQUIPMENT

Probably the most important step in controlling cooling tower scale and corrosion is installing effective automatic chemical proportioning and blowdown control equipment, including timer controllers. Cooling towers operate under widely varying load conditions; consequently, manually adjusted constant or varying feed and blowdown control does not usually provide acceptable results.

Many chemical feed systems employ a pH meter, conductivity, and corrosion rate or inhibitor measurements to control proportionate feed and blowdown; the following equipment is recommended for Army installations discussed in Table 4.

a. Chemical feed and blowdown control equipment based on pH meter, conductivity, and corrosion inhibitor or rate measurement is recommended for acid-treated systems.

b. Chemical feed is based on the conductivity measurement of water as registered on the makeup meter and blowdown control. If acid treatment will be applied, an acid-resistant vat, piping, and a pump will be required.

c. The quality of water registered on the makeup meter determines the chemical feed and the regulation

of the solenoid valve for blowdown control. If acid treatment will be applied, an acid-resistant vat, piping, and a pump will be required.

d. Conductivity measurement is applied to control both blowdown and chemical feed.

e. A slowly soluble polyphosphate is placed in plastic bags suspended in the towers. The treatment additions are monitored manually by checking water meter readings, and blowdown control is monitored by weekly conductivity testing and blowdown valve adjustment. This technique is generally used in small towers (less than 50 tons [45.3 MT]).

Since the best treatment control is based on measuring the makeup water's evaporation, blowdown, and windage loss, methods b and c are preferable. Generally, electriccontact water meters, including timers, have been specified for all air-conditioning equipment (centrifugal, reciprocating, or absorption) of 100 tons (90.7 MT) (or equivalent to evaporation of 150 gal/hr [616 l/hr]) or more. These water meters provide signals through adjustable timers to chemical pumps and solenoid blowdown valves to provide automatic treatment application and blowdown control. Method d is also used at many installations because it is less expensive; however, it is generally not accurate enough for acid feed control.

Avoid pH sensor controls because pumps tied to blowdown controllers are less accurate.

Most of the effective corrosion-inhibiting chemicals are toxic; in order to use them, all makeup should be applied at least 12 to 24 in. (30.5 to 61 cm) above the maximum water level or overflow to prevent possible back-siphonage into the drinking water supply. The entire circulatory system should be completely isolated from the city or potable water supply piping. In addition, corrosion inhibitors need a dual feed pump.

Monitoring the hardness, alkalinity, chloride, and corrosion inhibitor concentration by periodic water testing is necessary to insure that the correct chemical dosage and blowdown are being applied. Charging of the chemical vats should be checked frequently, as should the operation of the treatment equipment to insure that this equipment is operating properly. Commercial kits are available which test for hardness, alkalinity, chromate, and phosphonates.

Cooling towers constructed of wood are subject to chemical attack by high-pH water and high con-

tinuous residuals of strong oxidizing agents (such as chlorine of 0.5 ppm or greater), and to biological attack (fungi). These attacks may be either internal or external and may cause complete disintegration and collapse of wood tower structures; therefore, the towers should be closely inspected periodically. Inserting an ice pick into the wood to determine whether the wood is solid is one means of telling if there has been any internal attack.

To prevent chemical attack, towers can be constructed of wood pretreated with copper chromate and arsenate, or they can be sprayed with similar solutions after construction. Applying acid to lower the pH below 7.5 and avoiding continuous chlorine residuals above 1.0 ppm will prevent chemical attack.

4 SCALING

Scale Indices

Calcium carbonate is the predominant dissolved constituent of cooling tower waters. Temperature has a pronounced effect on the formation of scale; the solubility of calcium carbonate and other salts decreases as temperature increases. Figures 3 and 4 illustrate the loss of efficiency attributed to scaling.

In 1936, Langelier determined the scaling tendencies of water based on the solubility of calcium carbonate.¹ The pH of the saturated calcium carbonate solution can be calculated based on actual solubility of calcium carbonate at definite temperatures and dissolved solids contents. By comparing this value with the actual pH of the water to yield the saturation index, Langelier developed a way to indicate a water's scaling or corrosive tendency. The Langelier Index equals actual pH of the water minus pH_S, where

$$\text{pH}_S = A + B - [\log \text{Ca} + \log M] \quad [\text{Eq 5}]$$

Ca represents calcium hardness expressed as CaCO₃, and M represents methyl orange alkalinity expressed as CaCO₃. A represents the second dissociation constant and B the solubility product constant for calcium carbonate. These terms are functions of temperature and residues. The Langelier Saturation Index measures only

¹W. F. Langelier, "The Analytical Control of Anti-Corrosion Water Treatment," *Journal AWWA*, Vol 28, No. 1500 (1936).

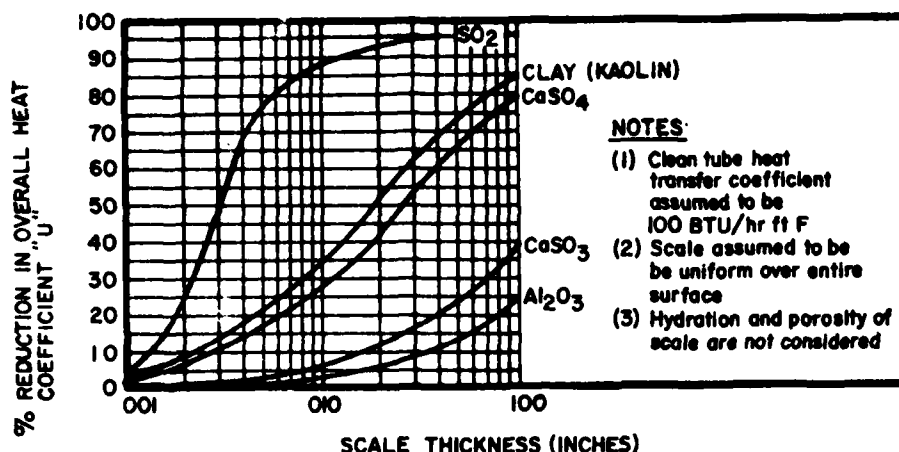


Figure 3. Heat transfer efficiency curve. (From J. M. Donahue and C. V. Sarno, "Pollution Abatement Pressures Influence Cooling Water Conditioning," *Materials Performance*, Vol 10, No. 19 [1971].)

the directional tendency or driving force of a water. It cannot be used as a quantitative measure.

The Ryznar Stability Index was developed to measure quantitatively the amount of calcium carbonate scale formed by water at a particular temperature.² The Ryznar Stability Index, R, is determined from the empirical expression:

$$R = 2(\text{pH}_S) - \text{pH} \quad [\text{Eq 6}]$$

A Ryznar Index of 6 or less indicates that the water has a definite scaling tendency; an index greater than 7 indicates that the water tends to be corrosive, and that scaling may not occur. The Ryznar Index also tells whether the threshold treatment with polyphosphate can be used; if the Ryznar Index is greater than 4.5, then the polyphosphates will hold the calcium in suspension.

A number of other indices, such as the driving force index and the momentary index, recognize a weakness in the Langelier Saturation Index as a direct criterion of the magnitude of excess calcium carbonate.³ The buffering effect of greater concentration of both calcium and alkalinity in a water probably also should be considered an important part of the water chemistry involved in providing a nonscaling and a stable noncorrosive water. The buffering effect is

the water's ability to maintain a potential or latent protective concentration after the deposition of a unit of calcium carbonate, and justifies specifying that a noncorrosive stable water should contain a certain minimum alkalinity and/or calcium.

Experience has shown that the greatest weakness in the Langelier Saturation Index occurs with water having a relatively low alkalinity and calcium content. Such waters have a saturation pH greater than 8.0 to 8.3. For some waters, the Langelier Saturation Index

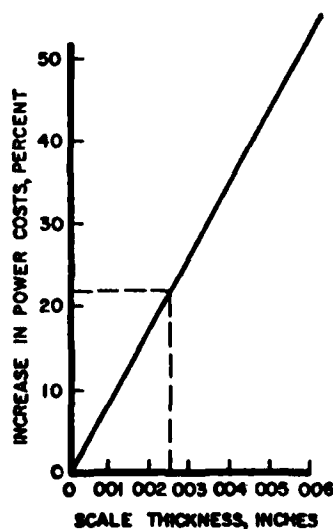


Figure 4. Impact of condenser-tube scale on power. (Reprinted with permission from POWER, May 1972.)

²J. W. Ryznar, "A New Index for Determining Amount of Calcium Carbonate Scale Formed by a Water," *Journal AWWA*, Vol 36, No. 472 (1944).

³*Handbook of Industrial Water Conditioning*, 7th ed. (Betz Laboratories, Inc., 1976).

may have to be +1.0 or more to establish the saturation pH for calcium carbonate. At this level, the buffer capacity is minimal. At the higher levels, the formation of complexes such as CaOH^+ , CaHCO_3^+ , MgCO_3^+ , and soluble CaCO_3 and MgCO_3 may be complicating MgCO_3^+ factors, since these complexes remove active concentrations of calcium and alkalinity from equilibrium considerations. Langelier Saturation Indices of about +0.2 or even 1.0 at room temperature may be required for a particular water supply, depending on the water use, water constituents, and temperature.

Analytical procedures fail to distinguish between these forms, which explains why one cannot rely entirely on Langelier Saturation and Ryznar Stability Index values to produce a stable, noncorrosive water. Regardless of these complications, the saturation and stability indices in conjunction with inspection (if pipe test sections may be used) are effective aids in producing stable, noncorrosive water.

The Langelier Saturation Index is the best way to control scaling. However, it must be calculated properly, and the pH must be measured at the site with a glass electrode.

Prevention of Scale

Scaling can be prevented with one of the following treatments:

1. Sodium zeolite softening to reduce hardness
2. Control of COC
3. Sulfuric acid to reduce alkalinity and pH
4. Slightly soluble polyphosphate
5. Sodium aminotrimethyl phosphonic acid (SATMP).⁴

Sodium zeolite ion exchange softening is effective in scale inhibition; however, the COC generally must be limited to 4 to 5 because of dust accumulations, overrun of softener capacity, or the dissolution of calcium carbonate from concrete basins. Zeolite softening often provides in the cooling tower system a high pH and alkalinity, which might lead to delignification of wood in wooden cooling towers. The high initial capital

costs of installing such softeners usually discourage this method of scale inhibition unless it must be used for other purposes, such as softening for domestic hot water.

Scaling can also be prevented by reducing the COC. For most exact calculations, the COC and blowdown requirements can be determined from the calcium and alkalinity of the makeup water as follows:

$$(\text{COC})_{\text{Max}} = \sqrt{\frac{110,000}{(\text{Ca}) \times (\text{M})}} \quad [\text{Eq 7}]$$

or

$$= \frac{2400}{\text{hardness H (CaCO}_3\text{)}}$$

where $(\text{COC})_{\text{Max}}$ is maximum cycles of concentration, and Ca, M, and H represent calcium hardness, methyl orange alkalinity, and hardness expressed as CaCO_3 . For example, if Ca and M are each 100 mg/l, then

$$(\text{COC})_{\text{Max}} = \sqrt{\frac{110,000}{(100)(100)}} = 3.3 \quad [\text{Eq 8}]$$

Therefore, this type of treatment is limited to the low-to medium-hardness waters having a $(\text{Ca}) \times (\text{M})$ less than 12,000, since operating below 3 COC is considered uneconomical.

The effective use of deposit control agents can almost completely prevent calcium carbonate precipitation unless the water is highly supersaturated because of the COC of hard makeup water. In such cases, the positive Langelier Saturation Index must be decreased by acid treatment. Complete elimination of the hardness by acid is not required; the hardness can be adjusted enough by bringing the acid-treated water into the effective range of surface active deposit control agents. Sulfuric acid is commonly used to reduce, not eliminate, water alkalinity. The alkalinity is reduced enough to achieve Saturation and Stability Indices that quantitatively indicate nonscaling conditions. Sulfuric acid treatment converts calcium bicarbonate to the more soluble and more stable calcium sulphate. If the water's sulphate content is too high, hydrochloric acid can be used to lower it. Acid treatment is the most effective scale inhibitor in hard waters (SP greater than 20,000). COC of 5 to 10 or more may be attained in most cooling waters. The COC limiting factor is often the dirt accumulation in the tower and the desired cleanliness of the condenser

⁴National Association of Corrosion Engineers, *Cooling Water Treatment Manual*, TPC Publication No. 1 (1971).

tubing. Operation at high concentrations (7.5 or greater) causes the evaporation of dissolved solids on cooling tower sills; too much accumulation may produce an undesirable appearance and eventually create air flow restrictions.

A widely used scale inhibitor is polyphosphate, which is applied at the rate of 0.5 to 5 ppm in the circulating water. This type of treatment uses polyphosphates below the stoichiometric values required for complexing calcium hardness and is termed "threshold" treatment. At these concentrations, polyphosphate inhibits the formation of scale from saturated solutions. The inhibition mechanism appears to be partly absorption on surfaces of growing crystals and partly inclusions in incipient crystal nuclei. These actions inhibit crystal nucleation and growth, thereby preventing scaling. The absolute limit of polyphosphate should be 7 ppm. Concentrations above 7 ppm will cause phosphate scale precipitation.

The use of molecularly dehydrated inorganic phosphates in aqueous systems causes serious problems because polyphosphates hydrolyze to form alkali earth metal orthophosphate, which causes scaling and fouling of the cooling tower system.

Unlike the molecularly dehydrated inorganic phosphates, phosphonates are stable, do not hydrolyze, and do not decompose to form alkali earth metal orthophosphate precipitates. Phosphonates are the preferred scale inhibitors in cooling towers. The mechanism of scale inhibition is the same as for polyphosphate. Often, the scale-inhibiting properties of phosphonates are enhanced when they are combined with polymers such as acrylates and surface active agents. However, if polymers are added, the dosage is critical, and close monitoring is required. The absolute limit of phosphonates is

$$\sqrt{\frac{110,000}{\text{Ca} \times \text{M}}}$$

otherwise phosphonate scale will precipitate.

When silica is present, the maximum COC has an absolute limit of $150 \div \text{Si}$ (ppm).

Scale formation in cooling tower systems is most serious in tubular heat exchangers or absorbers and in spray nozzles where the temperatures are highest. The simplest way to clean these areas is to apply inhibited muriatic acid or sulfamic acid. Only the condensers should be acid-cleaned; the addition of acid

to the entire system causes excessive wear to piping and other metal components which are not as scaled.

5 CORROSION INHIBITORS

Corrosion inhibitors can be anodic, cathodic, or organic.

Anodic Inhibitors

An anodic inorganic inhibitor restrains the anodic corrosion reaction, which is the dissolution of the metal. Anodic inhibitors reduce the available anodic area on the metal surface. In most cooling tower systems, reducing the anodic area does not reduce the corrosion rate proportionately. The entire corrosion attack is concentrated on any remaining exposed anodic sites, sometimes resulting in severe pitting. For anodic inhibitors to be effective, enough inhibitor to protect the entire area must be added.

Typical anodic inhibitors are sodium and potassium chromate and dichromate, polyphosphates, silicates, nitrites, ferrocyanides, and molybdates. Chromate salts are generally the most effective corrosion inhibitors. At low concentrations, chromate alone will promote pitting. Corrosion control is usually satisfactory if 100 to 300 ppm chromate content is added to open recirculating systems. Often, concentrations of 500 to 1000 ppm are required to control pitting in closed systems.

The addition of zinc, which is a cathodic inhibitor, to straight chromate, such as sodium dichromate, provides corrosion protection at lower levels of chromate concentration. The addition of zinc forms zinc hydroxide at cathodic sites, shields the metal from oxygen, and decreases the amount of time required to obtain a protective film. If phosphate is added, protection is further enhanced by the formation of zinc phosphate-zinc hydroxide combinations at cathodic sites. Adding phosphate reduces the amount of zinc required, but also requires lowering the pH level. Failure to consider the pH factor may cause the phosphate to precipitate as calcium phosphate. Certain organics such as lignosulfonates and synthetic polymers can be added to the chromate-zinc-phosphate formulations to improve their effectiveness and reduce pitting tendencies.

Although chromates are superior corrosion inhibitors, they are often pollutants; therefore, levels of

hexavalent chromium are set at a maximum of 0.05 ppm in areas where water potability is a concern. The maximum allowable hexavalent chromium that can be disposed of in sanitary sewers is 5 ppm. Since discharge of chromates contained in blowdown may not be acceptable at some installations, less effective corrosion inhibitors such as molybdate or phosphonate may have to be used. The application of low levels of chromate in minimum quantities of blowdown, and the dilution of chromates by the voluminous amounts of other wastes in the sanitary sewer, sometimes prevent a pollution problem.

Silicate pH levels must be controlled closely because their inhibition efficiency decreases above a pH of 7.5 and below a pH of 6.5.

Nitrites can also function as anodic inhibitors, but high (200 to 500 ppm) concentrations are required to satisfactorily inhibit corrosion in waters having a pH between 7 and 9. Below a pH of 6.5, nitrites decompose and cause localized attack of metals. Nitrites may also be converted to nitrates, which protect aluminum but not steel. When aluminum is present, nitrates and silicates must be added. If the pH of the water is alkaline, nitrites are not effective inhibitors for copper and its alloys. Usually, a copper inhibitor, such as mercaptobenzothiazole, is added to protect copper alloys and steels in cooling tower systems.

Insufficient amounts of anodic inhibitors may cause localized pitting. The different actions of polyphosphate and chromates as corrosion inhibitors have been united synthetically to combine their advantages. This method, called "dianodic" treatment, involves dual treatment of phosphates and chromates over a selected pH range. Superior protection and low cost have encouraged wide use of dianodic inhibitors. When it is not possible to establish or maintain the most effective ratio of phosphate to chromate without incurring deposition of calcium phosphate, zinc-chromate-phosphate can be used effectively.

Cathodic Inhibitors

Cathodic inhibitors restrain the cathodic corrosion reaction. Generally, any treatment which forms a coating on the cathodic surface because the pH at the cathodes is higher than it is in solution, functions as a cathodic inhibitor. Salts of metals such as zinc, nickel, manganese, and trivalent chromium which form slightly soluble hydroxides, oxides, and carbonates are cathodic inhibitors. Calcium carbonate is also a cathodic inhibitor, but its deposition cannot be con-

trolled to protect both hot and cold surfaces in a given cooling tower system. Hydroxide films formed by these materials at cathodic sites vary in thickness and continuity, sometimes allowing corrosion to proceed at the anode. Consequently, use of only a cathodic inhibitor is impractical.

Organic Inhibitors

Commonly used organic inhibitors are amines, amides, pyrides, carbonylic acid, esters, and mercaptans. Organic inhibitors are film-forming agents. Certain organic compositions, such as aminomethylene phosphoric acid (AMP), have greater temperature stability than polyphosphates.

The discharge of cooling system blowdown containing residual chromium often is not permitted. Nonchromate or nontoxic treatment formulations have been developed for use in these situations.⁵ Although several formulations contain no chromates, apparently no nonchromate inhibitor can match the effectiveness of the chromate-zinc-phosphate-organic blends. A second approach is to reduce the hexavalent chromium to a trivalent chromium form, and then increase the pH to precipitate the chromium and zinc as hydroxides. Ion exchange resins can be used to remove the chromium ions.

J. Kumar and J. P. Fairfax graded eight leading commercial systems in the laboratory and in plant tests.⁶ The overall cost and effectiveness of each system described in Table 5 was judged according to Kumar's index, which weighs the influence of scaling tendency, corrosion rate, and treatment cost. A laboratory-type heat exchanger was used to determine

⁵J. Kumar and J. P. Fairfax, "Rating Alternatives to Chromates in Cooling Water Treatment," *Chemical Engineering*, Vol 83, No. 111 (1976); T. C. Breske, "Testing and Field Experience with Nonheavy Metal Corrosion Inhibitors," *Materials Performance*, Vol 16, No. 17 (1977); C. S. Cone, "A Guide for Selection of Cooling Water Corrosion Inhibitors," *Materials Performance*, Vol 9, No. 32 (1970); J. M. Donahue and C. V. Sarno, "Pollution Abatement Pressures Influence Cooling Water Conditioning," *Materials Performance*, Vol 10, No. 19 (1971); A. S. Krisher, "Evaluation of Nonmetallic Cooling Water Inhibitors," *Materials Performance*, Vol 18 (1979), p 21; R. W. Lane, "The Case for Chromate in Cooling Tower Treatment," *Materials and Performance*, Vol 12, No. 9 (September 1973); A. Weissstuch and C. E. Schell, "Effectiveness of Cooling Water Treatments as Galvanic Corrosion Inhibitors," *Materials Performance*, Vol 11, No. 23 (1972).

⁶J. Kumar and J. P. Fairfax, "Rating Alternatives to Chromates in Cooling Water Treatment," *Chemical Engineering*, Vol 83, No. 111 (1976).

Table 5
Cooling Water Treatment Systems—How They Stand
 (From J. Kumar and J. P. Fairfax, "Rating Alternatives to Chromates in Cooling Water Treatment,"
Chemical Engineering, Vol 83, No. 111 [1976]).

System	Chemical Constituents	Concentration Maintained, ppm	Control pH	Actual Range of pH	Scaling Factor $\times 10^{-3}$	Corrosion Rate, Mils/Yr	Cost of Treatment, ¢/1,000 Gal of Water*	Kumar's Cost-Effectiveness Index**
A	Polyester corrosion-control agent + dispersant	50 20	8.0-8.5	7.7-8.6	14.46	20.5	25.8	2.78
B	Chromate-zinc base corrosion inhibitor + organic phosphate sequestrant	13 25	6.5-6.8	6.1-7.0	1.09	16.3	11.3	0.45
C	Pyrophosphate + organic phosphate sequestrant	25 25	7.5-7.8	7.2-8.6	5.97	28.2	12.4	1.44
D	Amino-phosphonate + polyacrylamide	40	None	7.6-8.5	6.28	19.0	15.8	1.37
E	Zinc-based corrosion inhibitor + organic polyelectrolyte	75 30	6.8-7.8	6.7-8.5	4.47	36.5	29.7	2.20
F	Organic polymer	40	7.0-7.5	7.0-8.1	16.79	43.2	18.8	3.69
G	Alkaline thiophosphate + phosphate ester + zinc	50	6.8-7.8	7.4-8.4	4.59	32.3	23.0	1.84
H	Alkaline organic-based inhibitor	50	None	7.8-8.7	3.36	58.4	37.8	2.72

*Based on 1971 prices.

**index = (Scaling factor \times corrosion rate \times cost of treatment)^{0.5}

scaling. Corrosion rates were measured by commercial corrosion rate meters of the linear polarization type. Kumar and Fairfax concluded that the best system (conventional chromate acid) had an index of 0.45. The next best treatments were amino-phosphonate plus polyacrylamide, and pyrophosphate plus organic phosphate sequester. The indices were 1.37 and 1.44, respectively, and were about three times higher than for chromate-acid treatment. Most of the systems in Table 5 are commercially available under various brand names.

6 CONCLUSIONS

The major causes of scaling, corrosion, and fouling in cooling tower systems are dissolved minerals of scale-forming salts.

The results of this research indicate that the most effective means of controlling damage to cooling tower systems caused by scaling, corrosion, and fouling are:

1. Use of increased rates of blowdown (in areas where water supplies are not limited) to reduce the scaling potential of circulating water by reducing COC.
2. Use of sulfuric acid treatment to inhibit scale formation by lowering the alkalinity.
3. Use of chemical formulations designed to inhibit scale and corrosion experienced by a particular installation.
4. Regular use of germicides or biocides when algae or slime growth is a problem, and elimination of sunlight on the water surface to reduce algae growth that is already present.

5. Installation of good automatic chemical proportioning and blowdown control equipment.

Use of all treatments and inhibitors should conform to USEPA regulations which limit the amount of agent that may be disposed of in sanitary sewers or near potable water supplies.

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APPENDIX: CORROSION PRINCIPLES

General

Almost all corrosion problems and failures can be associated with one or more of the following basic forms of corrosion: (1) general corrosion, (2) galvanic corrosion, (3) concentration cell corrosion, (4) pitting attack, (5) intergranular corrosion, (6) stress corrosion cracking, (7) de-alloying, and (8) erosion corrosion.⁷ Some or all of these types of corrosion are found in cooling tower systems. But all can be stopped or mitigated by a combination of six techniques: (1) coatings, (2) cathodic protection, (3) inhibitors, (4) proper material selection, (5) improved design, and (6) change of environment.

Corrosion occurs by an electrochemical process similar to that in a flashlight battery; i.e., the outer zinc electrode and the inner carbon electrode are connected through the ammonium chloride (NH₄Cl) electrolyte. When the outer circuit is completed, the zinc corrodes and generates a direct current.

The corrosion process requires an anode, a cathode, an electrolyte, and a metallic circuit connecting the anode and the cathode. In a plate of steel immersed in water, local anodes and cathodes are formed on the same metal surface. Metal dissolves at the anode where the corrosion current enters the electrolyte and flows to the cathode.



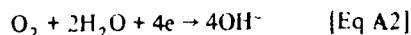
where *P* represents the metal involved

n is the valence of the corroding metal species

e is the electron charge.

This equation indicates that a loss of electrons, or oxidation, occurs at the anode of all corrosion reactions.

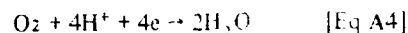
Electrons lost at the anode flow through the metallic circuit to the cathode and permit a cathodic reaction to occur. In alkaline and neutral aerated environments, the predominant cathodic reaction is:



The cathodic reaction which usually occurs in the de-aerated acids is:

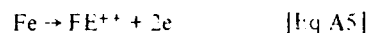


In aerated acids, the cathodic reaction could be:

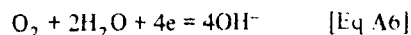


All these reactions involve a gain of electrons, or a reduction process.

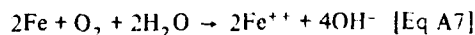
The number of electrons lost at the anode must equal the number of electrons gained at the cathode. For example, if iron is exposed to an aerated water, the anodic reaction is:



At the cathode, oxygen is reduced:



Since there can be no net gain or loss of electrons, two atoms of iron must dissolve to provide the four electrons at the cathode. The overall oxidation-reduction reaction is:



Following dissolution, ferrous ions (Fe⁺⁺) are generally oxidized to ferric ions (Fe⁺⁺⁺), which will combine with hydroxide ions formed at the cathode to give a corrosion product called rust, FeOOH or Fe₂O₃ × H₂O. The anodic dissolution of metal occurs electrochemically; insoluble corrosion products such as rust are formed by a secondary nonelectrochemical reaction.

The amount of metal or alloy dissolved electrochemically at the anode depends on the magnitude of the corrosion current. In accordance with Faraday's Law, every 96,487 coulombs (amps × seconds) dissolves one equivalent weight of the metal. The equivalent weight of metal is its atomic weight divided by the valence of the corroding species. The equivalent weight of iron, aluminum, and zinc would be 27.9, 9, and 32.7 g, respectively; aluminum dissolves as Al⁺⁺⁺). Thus, each ampere hour of corrosion current will dissolve 1.04 g of iron or 1.22 g of zinc.

⁷H. H. Uhlig, *Corrosion and Corrosion Control* (John Wiley and Sons, Inc., 1963); and M. G. Fontana and M. P. Greene, *Corrosion Engineering* (McGraw Hill Book Co., 1967).

If the effective electromotive force (EMF) driving a corrosion cell is E (in volts), the corrosion current depends on the value of E divided by R_T , where R_T is the cell or circuit resistance in ohms. Anything which decreases E or increases R will decrease the corrosion current. The total circuit resistance, R_T , depends on the resistance of the metallic circuit, R_m ; the resistance of the electrolyte, R_e ; the resistance of any anodic film, R_a ; and the resistance of any cathodic film, R_c :

$$R = R_m + R_e + R_a + R_c \quad [\text{Eq A8}]$$

The electrolyte must be sufficiently conductive to allow current to flow. Unless the environment has enough ionic strength, current flow and corrosion will not occur. Therefore, corrosion does not occur in petroleum-based liquids unless they contain sufficient moisture.

The resistance of the metallic circuit can often be neglected. However, it is important when the anode and cathode are physically remote. Anode and cathode film resistances are associated with the presence of corrosion products or any high-resistance coatings which might have been applied for corrosion control.

With zero current flowing, the initial corrosion self-potential, ϕ_{cor} , equals the difference between the potential of the cathode, ϕ_c , and the potential of the anode, ϕ_a :

$$\phi_{\text{cor}} = \phi_c - \phi_a \quad [\text{Eq A9}]$$

When a single metal is exposed to an electrolyte or a corrosive environment, local anodes and cathodes develop on the surface of the metal.

Anodic sites include

1. Areas of strained metal
2. Localized areas of low oxygen content in the electrolyte
3. Areas where the surface oxide film on the metal is broken
4. Impurities or precipitates in the metal
5. Grain boundaries
6. Regions of localized temperature

7. Grains where exposed crystallographic planes contain atoms of least close packing.

Cathodic sites include:

1. Areas of unstrained metal
2. Localized areas of high oxygen content in the electrolyte
3. Areas where the surface oxide film is intact
4. Impurities or precipitates in the metal; low hydrogen overvoltages
5. Grains where the crystallographic planes contain atoms of relatively close packing
6. Localized regions of low temperature; these micro-anodes and cathodes continuously change position, resulting in uniform corrosion.

It is generally difficult to obtain meaningful values for ϕ_c and ϕ_a when a single metal is exposed to a corrosive environment. Although ϕ_c can be estimated by the Nernst equation if the electrolyte's pH is known, ϕ_a approximations are complicated by the fact that the metal ion concentration in the immediate vicinity of the anodic sites is usually difficult to measure.

Single-electrode potential is created when the metallic material is placed in the electrolyte. Single-electrode potential cannot be measured directly because there is no cell; however, it can be determined for a metal using a reference electrode and a potentiometer or a high-resistance voltmeter. For these measurements, the reference electrode must have a constant and reproducible potential. A reference electrode widely used in the laboratory is the calomel half-cell. The silver-silver chloride reference cell is commonly used in saline environments, and the copper-copper sulphate reference cell is used extensively under field conditions.

The potential of various metals and alloys with respect to a reference cell arranged in decreasing order is called galvanic series. Certain materials can have two positions in the galvanic series e.g., Type 304 stainless steel. The more negative potential would be obtained when the material is in the active condition. The more noble potential would be obtained when the material is in the passive state. Metals and alloys are passive when they do not corrode in environments where they

should corrode. Although the cause of passivity is not completely understood, it is reasonable to believe that the presence of a thin surface oxide film (less than 100 angstroms thick), such as chromium oxide on stainless steel, is involved. The data in the galvanic series can be used to predict which metal or alloy should be the anode and which should be the cathode when two dissimilar metals or alloys are electrically connected and exposed to a conductive liquid such as water. For example, in seawater, aluminum ($E = 1.01$ V) would be the anode if it were metalically connected to a mild steel; similarly, magnesium would be anodic to copper.

Polarization

Although the initial corrosion cell potential (ϕ_{cor}) between two dissimilar metals or alloys can be estimated, the value of $\phi_c - \phi_a$ decreases as the current begins to flow. This decrease is caused by polarization. Polarization at the cathode causes ϕ_c to shift in the anodic direction; polarization at the anode causes ϕ_a to shift to the cathodic direction (see Figure 3). Both activation and concentration polarization can occur simultaneously.

Concentration polarization at the anode can be caused by the buildup of metal ions in the immediate vicinity of the anode surface. A limited supply of hydrogen ions or oxygen that causes an immediate reduction can produce concentration polarization at the cathode. In both cases, the corrosion rate would be diffusion-controlled. If anodic and cathodic concentration polarization occurred in the same corrosion cell, the corrosion current would depend on either the diffusion rate of metal ions *away* from the anodic surface, or the diffusion rate of hydrogen ions or oxygen *toward* the cathodic surface. (The slowest diffusion rate establishes the kinetics of the corrosion cell.) Concentration polarization is generally of primary importance when metals and alloys are exposed to aerated waters.

Activation polarization is a result of a slow step in the electrode reaction at the cathode or anode—e.g., the combination of mono-atomic hydrogen to form di-atomic hydrogen. Activation polarization generally establishes the corrosion current when metals and alloys are exposed to strong de-aerated acids.

Polarization is beneficial because it reduces the corrosion current. However, depolarization can increase the corrosion current to a value which is often orders of magnitude greater than that observed for a polarized cell. Increases in temperature and velocity can decrease polarization by increasing diffusion rates. The presence of oxygen can depolarize the cathode by reacting with hydrogen to form water, permitting additional hydrogen ions to be reduced; this requires more metal to be electrochemically dissolved at the anode.

Corrosion intensity at the anode is much more important than the amount of metal or alloy actually dissolved, because it provides a means of estimating service life. For a given corrosion current, the corrosion intensity increases as the anodic surface area decreases. The corrosion current density subtracted from the corrosion current (expressed as milliamps per square foot) determines the corrosion intensity. Corrosion rates are commonly reported in mils per year.

The corrosion current can be obtained by using a polarization technique sometimes called the Tafel extrapolation technique. Equipment is commercially available which can measure polarization resistance, as well as the Tafel extrapolation of corrosion current. Thus, the corrosion rate or the corrosion current density can be predicted. This technique is extremely useful for estimating corrosion rates of inaccessible submerged structures. Instruments which monitor the corrosion current density in circulating loops are available commercially. A more accurate method of monitoring corrosion is to insert preweighted coupons of metals in the circulating loop and remove them after a known exposure time.

The corrosion testing method (American Society for Testing and Materials [ASTM] D2688, method C) for distribution water is generally used to monitor the scale and corrosion in cooling towers. The flow of liquid in the testers is controlled by an orifice. This controlled flow is to be taken from the vertical inlet piping going to the top of the tower and is to be directed into the cooling tower basin. This flow is designed to provide the same velocity (4 feet per second) as that in the main circulating piping. Corrosion will be most prevalent under debris and leaves, so frequent cleaning is important.

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